STM on thin insulating films: a density matrix approach

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Outline

• **Scanning Tunnelling Microscopy** (STM) on thin insulating films
• **Interference** in electron transport measurements
• **Density matrix** approach to STM
• **Interference effects** in transport through Cu-Phthalocyanine
• **Conclusions** and **outlook**
STM on thin insulating films

Weak tip-molecule tunnelling coupling
Low molecule-substrate hybridization

sequential tunnelling
Visualization of molecular orbitals

Topography

Spectroscopy

Tautomerization and switching

Electro-mechanical entanglement

Double slit experiment: (London, 1801)

Phil. Trans. R. Soc. Lon., 94, 12 (1804)
Double slit with electrons: (Tübingen, 1961)

Aus dem Institut für Angewandte Physik der Universität Tübingen

Elektroneninterferenzen an mehreren künstlich hergestellten Feinspalten

Von
CLAUS JÖNSSON

Mit 14 Figuren im Text
(Eingegangen am 17. Oktober 1960)

A glass plate covered with an evaporated silver film of about 200 Å thickness is irradiated by a line-shaped electron-probe in a vacuum of 10⁻⁴ Torr. A hydro-carbon polymerisation film of very low electrical conductivity is formed at places subjected to high electron current density. An electrolytically deposited copper film leaves these places free from copper. When the copper film is stripped a grating with slits free of any material is obtained. 50 μ long and 0.3 μ wide slits with a grating constant of 1 μ are obtained. The maximum number of slits is five.

The electron diffraction pattern obtained using these slits in an arrangement analogous to Young’s light optical interference experiment in the Fraunhofer plane and Fresnel region shows an effect corresponding to the well-known interference phenomena in light optics.

Zeitschrift für Physik, 161, 454 (1961)
On the statistical aspect of electron interference phenomena

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(Received 29 May 1974; revised 17 October 1974)


Fig. 1. (a–f) Electron interference fringe patterns filmed from a TV monitor at increasing current densities.
Demonstration of single-electron buildup of an interference pattern

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(Received 17 December 1987; accepted for publication 22 March 1988)

The wave–particle duality of electrons was demonstrated in a kind of two-slit interference experiment using an electron microscope equipped with an electron biprism and a position-sensitive electron-counting system. Such an experiment has been regarded as a pure thought experiment that can never be realized. This article reports an experiment that successfully recorded the actual buildup process of the interference pattern with a series of incoming single electrons in the form of a movie.

Coherence and Phase Sensitive Measurements in a Quantum Dot

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(Received 10 November 1994)

Via a novel interference experiment, which measures magnitude and phase of the transmission coefficient through a quantum dot in the Coulomb regime, we prove directly, for the first time, that transport through the dot has a coherent component. We find the same phase of the transmission coefficient at successive Coulomb peaks, each representing a different number of electrons in the dot; however, as we scan through a single Coulomb peak we find an abrupt phase change of \( \pi \). The observed behavior of the phase cannot be understood in the single particle framework.

PACS numbers: 73.22.Dx, 71.45.-i, 72.80.Ey, 73.40.Gk

Time-Resolved Detection of Single-Electron Interference

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Received June 12, 2008

ABSTRACT

We demonstrate real-time detection of self-interfering electrons in a double quantum dot embedded in an Aharonov–Bohm interferometer, with visibility approaching unity. We use a quantum point contact as a charge detector to perform time-resolved measurements of single-electron tunneling. With increased bias voltage, the quantum point contact exerts a back-action on the interferometer leading to decoherence. We attribute this to emission of radiation from the quantum point contact, which drives noncoherent electronic transitions in the quantum dots.

Intramolecular interference: theoretical proposals

P. Sautet and C. Joachim

R. Stadler, et al.

G. Solomon, et al.

D. V. Cardamone, et al.

R. Baer and D. Neuhauser

S.H. Ke, et al.

T. Markussen, et al.
Experimental evidence


Fracasso et al. *JACS*, 133, 9556 (2011)
Destructive interference

Interference and dephasing

Source \[ \phi_1 \] Tunnelling barrier \[ \phi \] Collector

Nano junction

Source \[ \phi_2 \] Collector
Model of the STM junction

\[ H = H_m + H_{\text{sub}} + H_{\text{tip}} + H_{\text{tun}} \]

\[ H_m = \sum_{\alpha \sigma} \varepsilon_d d^\dagger_{d\alpha} d_{d\sigma} + \sum_{\alpha \sigma} \sum_{\beta \sigma} t^\dagger d_{\beta\sigma} d_{\alpha\sigma} + V_{e-e} \]

\[ H_{\text{sub}} = \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}\sigma} c^\dagger_{\vec{k}\sigma} S_{\vec{k}\sigma} \]

\[ H_{\text{tip}} = \sum_{\vec{k}_z\sigma} \varepsilon_{\vec{k}_z\sigma} c^\dagger_{\vec{k}_z\sigma} c_{\vec{k}_z\sigma} \]

\[ \varepsilon_{\vec{k}_z} = \varepsilon_0 + \hbar \omega + \frac{\hbar^2 k_z^2}{2m} \]

\[ H_{\text{tun}} = \sum_{\chi ki\sigma} t_{ki\sigma} c^\dagger_{\chi k\sigma} d_{i\sigma} + h.c. \]

No confinement in the x-y directions

Parabolic confinement in the x-y directions

It is a single particle operator

Molecular orbital

Sobczyk, Donarini, Grifoni.
Tunnelling amplitudes

\[ h = \frac{p^2}{2m} + v_m + v_{\text{sub}} + v_{\text{tip}} \quad t_{ki}^\chi := \langle \chi k \sigma | h | i \sigma \rangle \]

\[ Z_0 \quad 0 \quad d \quad Z_{\text{tip}} \quad Z_{\text{end}} \quad z \]

\[ \varepsilon_0 + \varepsilon_S \]

\[ \phi_0^S \]

\[ \text{substrate} \]

\[ \text{molecule} \]

\[ \text{LUMO} \]

\[ \text{tip} \]
Tunnelling amplitudes (ii)

\[ t_{ki}^\chi = \langle \chi k\sigma | \frac{p^2}{2m} + v_m | i\sigma \rangle + \langle \chi k\sigma | v_{sub} + v_{tip} | i\sigma \rangle \]

\[ = \varepsilon_i \langle \chi k\sigma | i\sigma \rangle \]

Valence atomic orbitals larger in the leads than in the molecule

More perpendicular nodal planes in the molecule than in the leads

\[ \psi_{\chi k}(\vec{r}) \phi_i(\vec{r}) \]

is shifted towards the molecule
Generalized Master Equation

• We start with the **Liouville equation**: \( \dot{\rho} = -\frac{i}{\hbar} [H, \rho] \)

• We define the reduced density matrix \( \sigma = \text{Tr}_{S+T}\{\rho\} \)
  which is block-diagonal in particle number, spin, and energy.

• We keep the coherences between **orbitally** degenerate states.

• The **Generalized Master Equation** is the equation of motion for \( \sigma \):

\[
\dot{\sigma} = -\frac{i}{\hbar} [H_{m}, \sigma] - \frac{i}{\hbar} [H_{\text{eff}}, \sigma] + \mathcal{L}_{\text{tun}} \sigma := \mathcal{L} \sigma
\]

**Coherent dynamics**  **Effective internal dynamics**  **Tunnelling dynamics**
Tunnelling Liouvillian

\[ H_{\text{tun}} = H_m - \mu_0 N \]

Grancanonical energy

\[ \mathcal{P}_{NE} = \sum_{\ell} |N E \ell\rangle \langle N E \ell| \]

Projector on the subspace of \( N \) particles and energy \( E \).

\[ \frac{1}{2} \sum_{\chi \tau} \sum_{i,j} \left\{ \mathcal{P}_{NE} \left[ d_{i \tau}^\dagger \Gamma_{ij}^\chi (E - H_m) f_{\chi}^- (E - H_m) d_{j \tau} + \right. \right. \]

\[ \left. \left. + d_{i \tau}^\dagger \Gamma_{ij}^\chi (H_m - E) f_{\chi}^+ (H_m - E) d_{j \tau} \right] \sigma^{NE} + h.c. \right\} \]

\[ + \sum_{\chi \tau} \sum_{ij E'} \mathcal{P}_{NE} \left[ d_{i \tau}^\dagger \Gamma_{ij}^\chi (E - E') \sigma^{N-1} f_{\chi}^+ (E - E') d_{j \tau} + \right. \]

\[ \left. + d_{j \tau} \Gamma_{ij}^\chi (E' - E) \sigma^{N+1} f_{\chi}^- (E' - E) d_{i \tau} \right] \mathcal{P}_{NE} \]
Single particle rate matrix

\[
\Gamma_{ij}^\chi(\Delta E) = \frac{2\pi}{\hbar} \sum_k (t_{ki}^\chi)^* t_{kj}^\chi \delta(\varepsilon_k^\chi - \Delta E)
\]

\[
H_{\text{eff}} = \frac{1}{2\pi} \sum_{NE} \sum_{\chi\sigma} \sum_{ij} \mathcal{P}_{NE} \left[ d_{i\sigma}^\dagger \Gamma_{ij}^\chi(E - H_m)p_\chi(E - H_m)d_{j\sigma} \right.
\]
\[+ d_{j\sigma} \Gamma_{ij}^\chi(H_m - E)p_\chi(H_m - E)d_{i\sigma}^\dagger \left. \right] \mathcal{P}_{NE}
\]

\[
I_\chi = \sum_{NE\sigma ij} \mathcal{P}_{NE} \left[ d_{j\sigma} \Gamma_{ij}^\chi(H_m - E)f_\chi^+(H_m - E)d_{i\sigma}^\dagger \right.
\]
\[- d_{i\sigma}^\dagger \Gamma_{ij}^\chi(E - H_m)f_\chi^-(E - H_m)d_{j\sigma} \left. \right] \mathcal{P}_{NE}
\]

Effective Hamiltonian

Current operator
Many-body rate matrix

The current is proportional to the transition rate between many-body states

$$R_{N E_0 \rightarrow N + 1 E_1}^{\chi \tau} = \sum_{i,j} \langle N + 1 E_1 | d_{i \tau}^\dagger | N E_0 \rangle \Gamma_{i j}^\chi(E_1 - E_0) \times$$

$$\langle N E_0 | d_{j \tau} | N + 1 E_1 \rangle f^+(E_1 - E_0 - \mu^\chi)$$

where

$$\Gamma_{i j}^\chi(E_1 - E_0) = \frac{2 \pi}{\hbar} \sum_k (t_{k i}^\chi)^* t_{k j}^\chi \delta(\epsilon_k^\chi - E_1 + E_0)$$

For uncorrelated and non-degenerate systems the many-body rate reduces to

$$R_{N E_0 \rightarrow N + 1 E_1}^{\chi \tau} = \Gamma_{\text{orb}}^\chi(\epsilon_{\text{orb}}) f^+(\epsilon_{\text{orb}} - \mu^\chi)$$

The constant current map is the isosurface of a specific molecular orbital.
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Dynamics in energy space

\[ H_G = H_m - \mu_0 N \]

\[ V_b = 0 \]

\[ \mu_N = E_N - E_{N-1} \]

Substrate tun.
Tip tunnelling

Particle Number

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Dynamics in energy space

\[ H_G = H_m - \mu_0 N \]

\[ V_b > 0 \]

\[ \mu_{N+1} = E_{N+1} - E_N \]

Gracanical energy

N - 1  N  N + 1

Particle Number

Tip tunnelling
Substrate tun.

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Dynamics in energy space

Grancanonical energy

\[ H_G = H_m - \mu_0 N \]

\[ V_b < 0 \]

\[ \mu_N = E_N - E_{N-1} \]

Tip tunnelling
Substrate tun.

Particle Number

N - 1  N  N + 1
Visualization of molecular orbitals

Topography

Dynamics in energy space

\[ H_G = H_m - \mu_0 N \]

\[ V_b = 0 \]

\[ \mu_N = E_N - E_{N-1} \]

Tip tunnelling
Substrate tun.
Dynamics in energy space

\[ H_G = H_m - \mu_0 N \]

\[ V_b > 0 \]

\[ \mu_{N+1} = E_{N+1} - E_N \]

Tip tunnelling
Substrate tun.
Dynamics in energy space

\[ H_G = H_m - \mu_0 N \]

\[ V_b < 0 \]

\[ \mu_{N+1} = E_{N+1} - E_N \]

Gracanonical energy

Particle Number

N - 1  N  N + 1

Tip tun.
Sub. tun.
Dynamics in energy space

Grancanonical energy

Particle Number

\[ \mu_{N+1} = E_{N+1} - E_N \]

Quasi-degenerate states

\[ \mu_S \quad \mu_N \quad \mu_{N+1} \]

Tip tun.

Sub. tun.

\[ \ell = 2 \]

\[ \ell = +1 \quad \ell = -1 \]

\[ D_{4h} \]

N - 1  N  N + 1
Interference blocking

Interference blocking

Topographical fingerprint

Experiment:
Cu-Pc on two-atomic-layer NaBr

W. Ho et al.
PRL 100, 126807 (2008)

Donarini, Siegert, Sobczyk and Grifoni
Interference blocking

Necessary conditions:

1. **Quasi-degeneracy** of the anionic ground state (e.g. Due to rotational symmetry);

2. **Electron affinity** approximately **equals** the (effective) substrate **work function**.

Fingerprints:

1. Strong **negative differential conductance** at **negative sample biases**;

2. **Flattening** of the **constant height current images** in the vicinity of the interference blockade regime.
Many-body tunnelling amplitudes

\[ H_G = H_m - \mu_0 N \]

Grancanonical energy

Particle Number

N

N + 1
Many-body tunnelling amplitudes

\[ H_G = H_m - \mu_0 N \]
Contact symmetry breaking

\[ |1'\rangle = a |1\rangle + b |2\rangle \quad \rightarrow \quad \gamma_{1' L} = a \gamma_{1 L} + b \gamma_{2 L} \]

\[
\begin{array}{c}
\frac{\gamma_{1 L}}{\gamma_{2 L}} \neq \frac{\gamma_{1 R}}{\gamma_{2 R}} \\
\exists \quad |1'\rangle \quad \gamma_{1' L} \neq 0 \\
|2'\rangle \quad \gamma_{2' L} \neq 0 \\
\end{array}
\]

Interference: decoupling basis

Degenerate anionic ground state $\Rightarrow$ Matrix form for the many-body tunnelling rate between the neutral and anionic ground states.

Angular momentum basis

\[ R_T^T = R_0^T \begin{pmatrix} 1 & e^{2i\phi} \\ e^{2i\phi} & 1 \end{pmatrix} \]

- Mixes angular momentum
- \( \ell = +1 \), \( \ell = -1 \)

Decoupling basis

\[ \tilde{R}_T^T = R_0^T \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \]

- One of the anionic state is decoupled from the tip

Substrate

\[ R_S^S = R_0^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

- Conserves angular momentum

\[ \tilde{R}_S^S = R_0^S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

Notice that the decoupling basis depends on the tip position.
Interference: current blocking

\[ V_b > -\Delta E_G / ec \]

Current

\[ V_b < \Delta E_G / e(1 - c) \]

No current

\[ \mu_T = \mu_0 - c eV_b \quad \mu_S = \mu_0 + (1 - c)eV_b \quad c \approx 0.9 \]
A new bottle-neck process

The depopulation of the blocking state via a substrate transition dominates the transport.
Conclusions

• We developed a **semi-quantitative model** for the description of “weakly coupled” STM junctions with π-conjugated molecules.

• The dynamics is described in terms of **many-body** transitions.

• Transport through **degenerate states** is associated to **electron interference** blockade at negative sample biases.

• Close to the interference blocking regime, substrate tunnelling dominates the transport and gives **flat constant height current maps**.
Interference + interaction

\[ H_G = H_m - \mu_0 N \]

Outlook

• Improve the description of the electron-electron interaction to include correlation effects (exchange, magnetic anisotropy…)

• Include molecular vibrations to investigate their impact on interference phenomena

• Study the effect of spin polarized current injection

• Include higher order tunnelling effects (co-tunnelling, Kondo)
Thanks

Benjamin Siegert  Sandra Sobczyk  Milena Grifoni

Thank you for your attention...

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Dynamics in a reduced space

\[
\begin{pmatrix}
\dot{\sigma}^N \\
\dot{\sigma}_c^{N+1\tau} \\
\dot{\sigma}_d^{N+1\tau}
\end{pmatrix} = 2R^T
\begin{pmatrix}
-2f_T^+ & 2f_T^- & 0 \\
f_T^+ & -f_T^- & 0 \\
0 & 0 & 0
\end{pmatrix}
+ R^S
\begin{pmatrix}
-4f_S^+ & 2f_S^- & 2f_S^- \\
f_S^+ & -f_S^- & 0 \\
f_S^+ & 0 & -f_S^-
\end{pmatrix}
\begin{pmatrix}
\sigma^N \\
\sigma_c^{N+1\tau} \\
\sigma_d^{N+1\tau}
\end{pmatrix}
\]

\[
I(\vec{R}_{\text{tip}}, V_b) = 2eR^S f_S^+ \sigma^N \left(1 - \frac{\sigma_c^{N+1\tau}}{\sigma_d^{N+1\tau}}\right)
\]

\[
\sigma^N = \left(1 + 2\frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} + 2\frac{f_S^+}{f_S^-}\right)^{-1}
\]

\[
\frac{\sigma_c^{N+1\tau}}{\sigma_d^{N+1\tau}} = \frac{R^S f_S^+ + 2R^T f_T^+}{R^S f_S^- + 2R^T f_T^-} \cdot \frac{f_S^-}{f_S^+}.
\]
Constant current maps calculated at working currents: $I = 3.15, 3.075, 3.0, 2.925$, and $2.85 \text{ pA}$